Renewable and Sustainable Energy Reviews 15 (2011) 4002–4012

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review of carbon dioxide capture and utilization by membrane integrated microalgal cultivation processes

Muhammad Syukri Abd Rahaman [a,c], Li-Hua Cheng [b,*], Xin-Hua Xu [b], Lin Zhang [a], Huan-Lin Chen [a]

[a] Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, PR China
[b] Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, PR China
[c] Department of Chemical and Process Engineering, National University of Malaysia, 43600 Selangor, Malaysia

ARTICLE INFO

Article history:
Received 12 January 2011
Accepted 5 July 2011
Available online 21 August 2011

Keywords:
Microalgae
CO_2 distribution
CO_2 capture
Photobioreactor
Membrane separation

ABSTRACT

The capture of carbon dioxide (CO_2) from the air for microalgal cultivation has received increasing interest since it allows advantages that do not only reduce the amount of CO_2 already added to the air, but it is also more economical due to the accessibility of air, there are no regeneration requirements and it is a safe method that can help enhance microalgal growth. In order to capture CO_2 from the air, it is necessary to deal with CO_2 emissions from all sources in an atmosphere. Interestingly, the capture unit and microalgal culture can be located at any favorable site. Although a number of photobioreactors have been proposed with a CO_2 distribution system, the consequence of CO_2 losses is still being ignored. Thus, capturing CO_2 from the air via an integrated separation process in a photobioreactor is required for microalgal cultivation. Among the four available separation technologies, the membrane separation process would offer a safe, reliable and low cost method for CO_2 capture. Thus, this method of separation can be considered as a key factor in accelerating the development of a CO_2 enrichment process from the air for microalgal cultivation.

Contents

1. Introduction

Microalgae are photosynthetic microorganisms that convert light, water and nutrients (carbon dioxide (CO_2), nitrate, etc.) for commercial and industrial purposes. The cultivation of microalgae for health benefits has extraordinary potential, and their use in the development of future forms of renewable energy is of particular interest [1–3]. They can be cultivated under extreme agro-climatic conditions and are able to produce a wide range of value-added bio-products. Certain microalgae are effective in the production of hydrogen and oxygen through the process of biophotolysis, while others naturally manufacture hydrocarbons that are suitable for direct use as high-energy liquid fuels [4].

Microalgae have a large capacity for producing lipids for biofuel. They have high potential as biofuel feedstocks because of their high rate of productivity. Microalgae, in addition, are receiving increase attention in the search for sustainable and profitable biofuel feedstocks. Interestingly, the productivity of microalgae is greater than

* Corresponding author. Tel.: +86 571 87953802; fax: +86 571 87953802.
E-mail address: chenglihua@zju.edu.cn (L.-H. Cheng).

1364-0321/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.rser.2011.07.031

that of the world's vegetation product [5,6]. Although microalgal productivity is not limited to the production of biofuel, the ability to transform microalgae into biofuel is an escalating science that is significant to the renewable energy industry, even though some difficulties such as reactor limitations and low lipid contents must be solved as a priority [7]. It is well known that biofuel is clean burning, non-toxic and carbon neutral to the environment. This clean biofuel could control the problem of global warming. Several studies have documented the significance of emission improvements in biofuel over petroleum fuel and this may be an important benefit for urban air quality [8,9]. Furthermore, it is believed that the alteration of fuel consumption from fossil fuel to biofuel will come through the development of innovative microalgal plants.

Microalgae do not require a large area for cultivation: only 3% of the area required by vegetation is needed [4,9]. Including these advantages, Umdu and co-workers [10] reviewed the potential of microalgae for the production of biofuel and concluded that microalgae are promising because:

(a) they grow rapidly, with cells multiplying quickly within 24 h;
(b) improvements in their lipid contents can be made by changing medium conditions, such as light and nutrients;
(c) they can be harvested on a large scale with continuous production for the continual supply of oil;
(d) salty or low quality water can be used for growing microalgae;
(e) the carbon source for culture growth is easily acquired, for instance CO_2 from atmospheric air;
(f) biofuel from algal lipids is non-toxic and highly biodegradable;
(g) microalgal biofuel production is up to 300 times greater compared to traditional crops on the basis of area.

Despite the potential of microalgae as a biofuel resource, many challenges have impeded the development of microalgal biofuel technology to commercial viability for sustainable production. Important factors such as light, nutrients, metabolic engineering and economic considerations need to be addressed for microalgal cultivation [4]. Previously, some studies revealed the fact that CO_2 also plays an important role in microalgal development and, in particular, a number of engineering studies were provided on the photosynthetic systems of microalgae [8,9]. These systems are the best near-to-intermediate term solution for reusing carbon emissions in the energy sector and, consequently, they may reduce the atmospheric CO_2 concentration. Based on these biological systems, diverse biochemical engineering processes are being carried out in which the metabolism of these photosynthetic microorganisms converts nutrients such as CO_2, water and light energy into natural molecules to obtain energy [9,10].

Conventionally, the microalgal cultivation process has to be exposed to the air to obtain CO_2 from the atmosphere for cell growth and to increase the added value of the microalgae. Carbon dioxide is available under two major conditions: on the one hand, only 0.03–0.06% CO_2 can be offered as normally contained in atmospheric air [11–13], whereas on the other hand, elevated CO_2 concentrations can be considered, for instance, in flue gas or mixed gas (6–15% CO_2) [14–17], which has become a major focus of the environmental agenda. However, in order to grow microalgae continuously, the CO_2 provided should be safe and commonly available in order to trigger microalgal production. Unlike atmospheric air, flue gas may comprise amounts of toxic gases such as NOx and SOx, which should be dealt with prior to the cultivation process [18]. Therefore, capturing CO_2 from the air is probably an appropriate method for providing a carbon sink from which CO_2 can be consumed by microalgae during photosynthesis [19].

In this paper, the requirements of capturing and enriching CO_2 from the air for microalgal cultivation will be highlighted. We would like to discuss the existing technologies of CO_2 distribution systems that incorporate CO_2 capturing technologies for microalgal cultivation and the improvement of environmental conditions. In order to be selected for reliable CO_2 enrichment, these separation processes should offer several practical advantages including high selectivity at a low cost with the potential to exert a positive influence on the development of microalgae.

2. The importance of carbon dioxide capture

Carbon dioxide (CO_2) is essential to photosynthesis and other photoautotroph processes. However, in recent years, carbon dioxide has become the focus of attention because of its position as the primary greenhouse gas. It is released into the atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. Moreover, deforestation, which liberates the carbon stored in trees, as well as human activities in chemical processing, results in more CO_2 being released.

During this time (since pre-industrial age), the atmospheric concentration of CO_2 has increased from 280 ppm to more than 370 ppm currently [20,21]. More specifically, coal produces approximately 50% of the CO_2 emissions from fossil fuels (oil 37% and gas 13%) [22]. Global CO_2 emissions from fossil fuels increase by more than 4% each year. The increase in CO_2 emissions is proportional to the world's population growth rate, which is estimated to increase exponentially by 1.35 [23]. As a result, the CO_2 concentration in the air is expected to increase by 75 ppm during 2000–2050 [22]. The increase of 100 ppm since the pre-industrial age has already caused about 75% of the anticipated 1 °C warming [24]. Hansen et al. [22] predicted that levels of CO_2 greater than 450 ppm would be "dangerous" and could be highly destructive to the world's global climate. Thus, these phenomena indicate that the capture of CO_2 from the air will be developed as an important long-term air treatment strategy for managing climate risk.

Most of the carbon capture storage (CCS) technologies only mitigate CO_2 from fossil fuel or large fixed-point sources such as power plants [25,26]. Although technologies to capture CO_2 from the flue gas of coal-fired power plants can cut emissions, these technologies still cannot reduce the climate risk posed by the CO_2 that has been added to the air. Unlike the mitigation of CO_2 from flue gas, the advantage of capturing CO_2 from the air is that there is no need to extract all of the CO_2 out of the air [27]. Carbon dioxide gas is still required in the air to prevent the earth's temperature becoming lower than the freezing temperature of 273 K [28]. Moreover, the necessity of capturing CO_2 from the air is due to its ability to remain in the air. The percentage of CO_2 remaining in the air (CO_2 (%)) can be calculated using the Bern carbon cycle model (Eq. (1)), where t is time in years [22]. Using this equation, it has been shown that the level of CO_2 in the air will still remain at approximately 0.33% of the initial CO_2 concentration after 100 years and at about 0.2% after 1000 years or even after 2000 years. However, other emission gases in flue gas such as SOx and NOx have a relatively short lifetime in the air (i.e. hours to days for NOx and 14–20 days for SOx) [29,30]. Consequently, the remaining fraction of CO_2 will accumulate and create elevated levels of CO_2 in the air. Hence, this situation will pose long term climate and geochemical risks. In order to stabilize the concentration of CO_2, it is necessary to deal with CO_2 emissions from all sources in an atmosphere. Thus, capturing CO_2 from the air could be favorable for halting the increase in atmospheric concentrations of greenhouse gases and for avoiding the dangers of climate change [25]. It also seems to be significant for avoiding the next predicted 1 °C temperature rise. In addition, the capture of CO_2 from the air can compensate for any emitted CO_2 by capturing CO_2 at a different location and time. The capture unit can be located at a favorable sequestration site and the need for extensive CO_2-transportation infrastructure can be avoided [26].

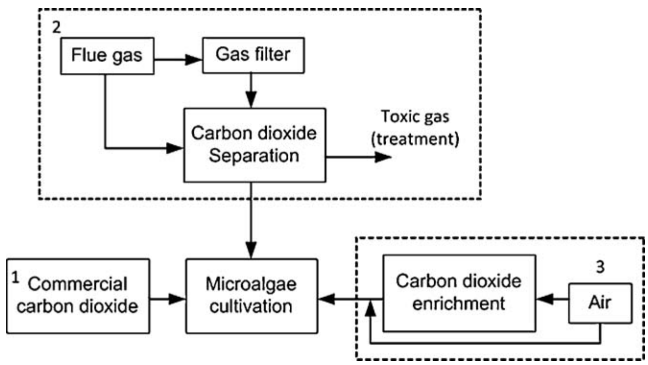


Fig. 1. Different carbon dioxide sources for cultivation of microalgae.

Therefore, the unit can be taken to places far away from populated cities. In addition, the large-scale capture of CO_2 from the air could reduce the concentration of CO_2 in the atmosphere. Subsequently, the CO_2 capturing process will treat the emission of greenhouse gases comprised of CO_2.

$$CO_2(\%) = 18 + 14^{e-t/420} + 18e^{-t/70} + 24e^{-t/21} + 26e^{-t/3.4} \quad (1)$$

The capture of CO_2 can be engineered by capturing CO_2 from ambient air whether for the disposal of CO_2 or for the benefits of its reuse [8,9,27]. Additionally, over the long term, the ability to capture CO_2 from the air should not be viewed only as an essential tool for managing carbon climate risks, but also as a source for the generation of renewable energy, such as by using microalgae. This is because the process of recapturing CO_2 from the air completes the carbon cycle in the atmosphere. This way, it can serve as a beneficial feedstock for microalgal cultivation. Moreover, studies have also shown the potential of microalgae in adsorbing a portion of anthropogenic CO_2 as a fixed organic carbon source to be used in the photosynthetic process [31,32].

3. Carbon dioxide for microalgal cultivation

3.1. Correspondence between the concentration of carbon dioxide and microalgal cultivation

Generally, there are three sources of CO_2 that can be used for cultivating microalgae [7,11,14]. Fig. 1 shows the different sources of CO_2 for microalgal cultivation. Although commercial CO_2 is widely available, it should not be a priority for the microalgal cultivation process since it is not continuously available [33,34]. Moreover, the consumption of commercial CO_2 can increase microalgal production costs and decrease the potential of using microalgae to mitigate CO_2 levels in the air. It is preferable for this high purity CO_2 gas (up to 99%) to be mixed with air at a certain ratio (i.e. 1% CO_2). This mixing can reduce the carbonate accumulation that decreases CO_2 consumption by the ribulose bisphosphate carboxylase oxygenase (RuBisCO) enzyme in the bulk liquid [33]. The RuBisCO enzyme is responsible for the consumption of CO_2, serving as the biological carbon sink. It is necessary to convert CO_2 into 3C-phosphoglycerate (3-PGA) molecules in the Calvin Cycle during the day because ribulose 1,5-bisphosphate (RuBP) is not produced in the dark. However, insufficient amounts of CO_2 will cause binding of the RuBisCO enzyme to oxygen (O_2) rather than CO_2. This process is called photorespiration. Therefore, in order to provide an adequate amount of CO_2 for the RuBisCO enzyme, the optimal pH of CO_2 in the bulk liquid must be in the range of pH 8.5–10.3 [33].

Secondly, flue gas (or mixed gas) has also been found to be another source of CO_2 for microalgal growth [35]. Normally, the concentration of CO_2 in flue gas is around 10–15% and is only available in limited places such as near urban and industrial areas [25]. Furthermore, besides these limited places and availability, prior to CO_2 dispersion into the microalgal cultivation process, the flue gas needs another treatment. According to Lee and Lee [18], microalgal growth becomes inhibited by the increasing injection rate of flue gas into the culture medium. The most important inhibitory compounds to microalgal cells are NOx and SOx in flue gas [18]. The presence of NOx and SOx gases reduces the pH to levels lower than minimal (pH 8.5) in the bulk liquid. In addition, the most CO_2-tolerant microalgae can survive in conditions lower than 50 ppm NOx and SOx [36,37]. Therefore, controlling the pH level in the microalgae medium is necessary for minimizing the toxicity of the CO_2 supplied, otherwise the microalgal population will be harmed and become reduced in number [7]. A number of research studies have been carried out in attempts to overcome the effects of NOx and SOx [37–39]. They have controlled the pH by introducing high CO_2 concentrations (15–20%) or by providing sodium hydroxide (NaOH) to the culture system. However, controlling the pH level in the culture system is only effective for some microalgae, such as *Chlorella littorale Chlorella* HA-1, *Synechocystis* sp., *Chlorella caldarium* and *Chlorella* KR-1 [38]. It was found that acidophilic microalgal strains were not inhibited by 50 ppm NOx and growth well in 50 ppm of SOx aeration [38]. Therefore, to provide an excellent microalgal growth, CO_2 from atmospheric air could be a significant source of harmless CO_2 for microalgal cultivation.

Although increases in the concentration of CO_2 cause global warming, the current atmospheric concentration of CO_2 is still not adequate to sustain a viable colony of the proposed microalgae. For example, *Chlorella vulgaris* grows very slowly when only utilizing 0.035% CO_2 in the air [35]. Our previous work [33] found that the maximum growth rate of *Chlorella vulguris* for CO_2 fixation is obtained when the concentration of CO_2 in the aeration gas is around 1%. Besides this, microalgae such as *Chlorella* sp. also have a good tolerance toward high CO_2 concentrations and can grow in CO_2 concentrations in excess of 5% [39]. Moreover, it was found that the growth of this culture remained stable each day, even though high concentrations of CO_2 (10–15%) were introduced into the culture system [11]. It has also been revealed that *Chlorella* sp. can grow in up to 40% CO_2 at pH 5.5–6.0 and at 30 °C [40]. According to Chiu et al. [11], a high CO_2 concentration is beneficial, especially when cultivating high density cultures such as *Chlorella* sp. (8×10^6 cells mL^{-1}), in order to enhance the availability of CO_2 as the carbon source. Furthermore, a study on the effects of microalgal populations under low and high CO_2 concentrations found that environmental CO_2 gas, which is found at concentrations up to 30%, can increase primary productivity in natural populations of microalgae [35]. Hence, several studies have shown the importance of the concentration of CO_2 in algal cultivation, which can serve as an excellent tool for CO_2 biofixation, reducing the level of CO_2 in the air [18,41].

Normally, when research into CO_2 fixation by microalgae is conducted, biomass production is the most important product that should be observed [42]. This biomass production is used to indicate microalgal productivity. For example, a high level of biomass with a high lipid or hydrocarbon content can produce better biofuel productivity. However, there are still some inconsistencies in the production rates reported in the literature (Table 1). Some strains can only tolerate low concentrations of CO_2 in the gas stream (below 2%), whereas some can tolerate concentrations greater than 2% CO_2 (2–15%) for high levels of lipid production. It is believed that the optimum consumption of CO_2 and the high lipid or hydrocarbon content of microalgae provides the best circumstances for the production of liquid biofuel [4,43,44]. Moreover, these important products of microalgae can exceed up to 70% of their dry mass, even though algae with a lipid content of around 30% is more common [4]. According to Table 1, although there is interest in the CO_2

Table 1
Microalgae biomass production at a certain CO_2 concentration.

Microalgae	CO_2 initial	CO_2 fixation	Biomass Production ($mg\,L^{-1}\,d^{-1}$)	Lipid productivity ($mg\,L^{-1}\,d^{-1}$)	References
Aphanothece microscopica Nägeli	15%	~99%	540–770	~40–60	[43,48]
Botryococcus braunii	0.5–10%	–	40–750	40–480 (hydrocarbon)	[47,49]
Chlorella kessleri	6–18%	~4%	67–87	–	[50,51]
Chlorella protothecoides	2%	–	2860	417	[13,52]
Chlorella sp.	2–15%	16–58%	760–870	–	[11]
Chlorella vulguris	~2%	74%	30–45	15–25	[12,45]
Nannochloropsis oculata	2–15%	~13–55%	490	80–150	[53]
Platymonas subcordiformis	<10%	~3%	44	–	[54,55]
Scenedesmus obliquus	6–18%	14–28%	~60–160	10–80	[50,56]
Spirulina plutensis	4%	61.5%	350	4–9	[34]
Spirulina sp.	6%	~5–9%	125–280	5–20	[2,51]
	>12%	1–5%			

biofixation of *Aphanothece microscopica* Nägeli, *Botryococcus braunii* and *Chorella vulguris* have higher hydrocarbon and lipid contents, respectively, which almost comprise 60% of their dry weight, especially under nitrogen depletion [45–47]. These findings illustrate the fact that research on CO_2 fixation by microalgae can yield a high lipid content coupled with a high volume of productivity under the appropriate cultivation conditions. With a high CO_2 requirement, microalgae can be annually harvested and collected as biofuel energy source.

However, the processes for production and biological flue gas cleanup are still under development. There are several problems, such as the biomass productivity being too low and the CO_2 utilization not sufficient for meeting industrial challenges. Consistent with the results of Chisti [4], it has been shown that reaching a stable and high level of productivity from microalgae is difficult, even though a number of efficient strategies are developed. Thus, a rigorous technology should be adopted in order to optimize the recovery and enhance the distribution of CO_2 in microalgal cultures. Consequently, the production of biofuels by microalgal cultures could be increased to be competitive with petroleum-derived fuels.

3.2. Carbon dioxide distribution in the photobioreactor

Various methods have been developed in order to isolate and cultivate microalgae in the laboratory, as well as outdoors, on a large scale of production [4]. In the conventional production process, an open pond is preferable for microalgal growth [57,58]. An open pond bioreactor allows the penetration of CO_2 from the atmosphere for microalgal cultivation [7]. However, the open pond system is more susceptible to evaporative losses and CO_2 diffusion into the atmosphere. In addition to CO_2 losses, contaminants, which are created by unnecessary algae or protozoa in the open pond system, make this system inefficient [59,60]. Thus, in order to overcome this difficulty, the pond must be covered or transparent material must be used, as indicated by Jorquera et al. [61]. This covering allows an extension of the growing period of the microalgae. This in turn facilitates the requirement of CO_2 in the medium and maintains a high temperature at night. Moreover, covering an open pond can trap the CO_2 losses, resulting in improved microalgal populations and biomass productivity [62,63]. In addition, environmental conditions, especially CO_2 distribution, can also be controlled to benefit growth of the microalgae [64,65].

However, essential issues such as the minimization of CO_2 losses must also be addressed. Moreover, the local CO_2 concentration in the culture medium should not drop below the critical CO_2 value required for microalgal cultivation at any point. When the CO_2 concentration in a microalgal medium becomes too limiting, photosynthesis is restricted [66]. Thus, in order to enable excellent biomass production and the efficient mass transfer of CO_2, the microalgal cultivation system must be equipped with a photobioreactor. The proper penetration of CO_2 into the photobioreactor will enable the microalgae to easily consume the carbon atoms and the culture will accumulate to form biomass [67,68]. For instance, Dutil [69] designed a photobioreactor that includes a gas channel for cultivating photosynthetic organisms. In his system, CO_2 is supplied by a gas dispenser extending to the bottom floor of the container. This gas dispenser is generally parallel to the light-emitting tube and supplies CO_2-enriched air to the container. Moreover, placing the gas dispenser at the bottom of the reactor can enhance mixing of the CO_2 with the microalgae. Besides this, a similar cultivation process has also been designed which distributes gas through a parallel sparger [70]. The sparger is comprised of plurality pin holes that provide significant CO_2 dispersion and also reduces the mixing time. Furthermore, Contreras et al. [71] reported that improvements of the CO_2 mixing time can diminish the CO_2 gradient in the medium and increase the availability of CO_2 for the microalgae. As a result, this improvement enhances the specific growth rate of microalgae for a higher biomass concentration.

In 2007, another photobioreactor invention was introduced by Levin [72]. In his invention, CO_2 is supplied by introducing a column for gas distribution to the microalgae that includes oxygen (O_2) stripping to avoid O_2 saturation during photosynthesis. It is known that O_2 saturation in the microalgal medium can inhibit microalgal growth even when an elevated concentration of CO_2 is supplied [41,73]. Furthermore, the gas distribution channels must be arranged in parallel to each other in order to maximize CO_2 consumption for microalgal growth [72]. However, those inventors have only designed CO_2 distribution systems that bubble CO_2 into the culture medium. This is not particularly effective in terms of mass transfer. The overall mass transfer coefficient of CO_2, K_La (CO_2), can be calculated by multiplying the overall mass transfer coefficient of O_2, K_La (O_2), by a factor of 0.91 [41]. The K_La (O_2) can be evaluated using the following O_2 mass balance equation (Eq. (2)) [74]:

$$\frac{J_L}{60} = ([O_2]_{out} - [O_2]_{in}) = VK_La(O_2)([O_2^*] - [O_2])_{lm}(1 - \varepsilon) \tag{2}$$

where J_L is the liquid volume flow rate ($L\,min^{-1}$), ε is the gas hold up, which is determined by the volume expansion method (Eq. (3)) [75], where V is the volume of the fluid in the reactor with aeration, and V' is the volume of the fluid without aeration. $[O_2]$ and $[O_2]^*$ are the dissolved O_2 concentration and the equilibrium concentration of O_2 in the liquid ($mol\,L^{-1}$) and $([O_2^*] - [O_2])_{lm}$ is the logarithmic mean driving force for O_2 transfer ($mol\,L^{-1}$):

$$\varepsilon = \frac{V - V'}{V} \tag{3}$$

The value of the gas hold up (ε) is proportional to the overall mass transfer coefficient K_La (Eq. (2)). According to our experiment effort [41], bubbling gas has a smaller gas hold up than the membrane sparger. This is because bubbling gas has a larger bubble

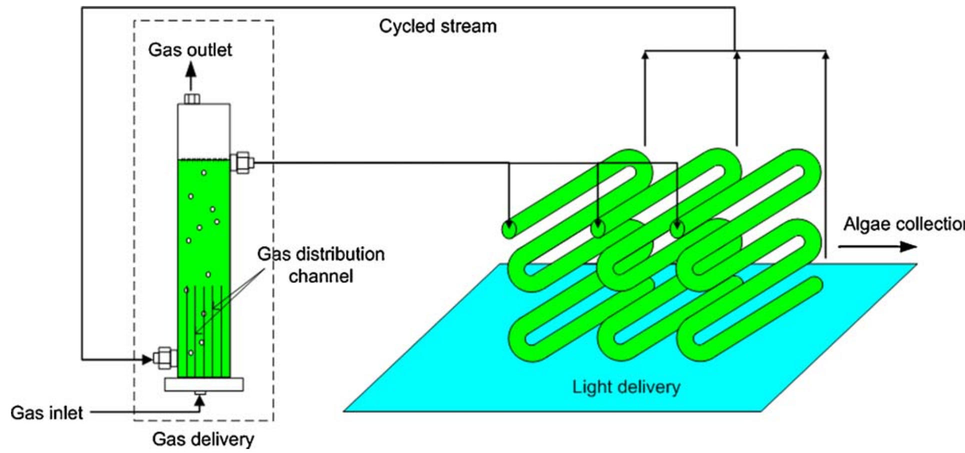


Fig. 2. Airlift photobioreactor with gas and light delivery system.

diameter in the bulk liquid. A larger bubble diameter will have a smaller velocity and a small expansion volume. Consequently, the value of the gas hold up will be reduced, as calculated by Eq. (3). Thus, it is preferable to integrate the membrane into the photobioreactor system to improve the CO_2 mass transfer in an algae medium. It has been demonstrated that a membrane such as a silicone tube will enlarge the contact area between the CO_2 and the algae medium by diffusing the gas through the membrane [76]. In contrast to the conventional CO_2 bubbling process, the K_La for CO_2 transfer using the membrane is reported to be 50% greater [77].

In our previous works, we also attempted to enhance the CO_2 distribution by applying a membrane sparger in an airlift photobioreactor [33,41,78]. In these works, various membrane fiber types and distribution specifications were used in the photobioreactor, such as membrane sparger, a membrane contactor and bubbling gas. The results showed that the photobioreactor using the membrane contactor provided the smallest value of K_La (CO_2) in the range of 0.0007–0.0082 s^{-1}. This is because in this system virtually no bubbles permeated into the medium. Meanwhile, by using bubbling gas, the K_La (CO_2) was slightly increased from 0.0056 s^{-1} to 0.0180 s^{-1}. However, the K_La (CO_2) of this bubbling gas was still lower than that of the membrane sparger. The membrane sparger had the highest K_La (CO_2) (0.0692–0.1289 s^{-1}) and consequently accelerated the mass transfer of CO_2 into the culture medium [41]. The process with the large K_La (CO_2) coefficient had the shortest CO_2 transport time, which may have resulted in an easier CO_2 dispersion into the medium. Moreover, a membrane sparger can distribute CO_2 at a rate up to five times faster than other specification distribution rates [78]. Thus, the membrane sparger seems to be a promising device that can be combined with the microalgal cultivation process in order to increase CO_2 consumption. In summary, the closed membrane sparged photobioreactor can be set up using the following criteria:

(a) It must be made from tough and durable materials that accommodate easy control in order to avoid any contamination.
(b) It must be easy to install with an appropriate CO_2 distribution system while avoiding O_2 accumulation.
(c) The distribution system should provide an acceptable CO_2 concentration with maximum dispersion for consumption by the algal culture.
(d) The provided sparged membrane system must also be able to control membrane fouling problems.

In agreement with Greenwell et al. [79], the photobioreactor with an excellent gas distribution system must also provide an optimum light source (λ = 400–700 nm) for culture growth. The light permeable vessel of a complete photobioreactor system equipped with gas and light delivery systems is illustrated in Fig. 2. In this figure, the air and CO_2 are supplied to the cultures through a gas supplement port at the bottom of the gas delivery system. The gas is then distributed through the channels for dispersion. These gas distribution channels can be made of dead-end materials such as a membrane or a silicone tube comprised of micropores in order to reduce the CO_2 bubble size for maximum dispersion throughout the culture medium. Furthermore, in this system, the generated O_2 gas and the reduced CO_2 gas are released from the top of the column. Interestingly, the light delivery in this system is separated from the gas delivery in order to reduce the light reflecting problem which is due to bubble accumulation as indicated previously [78].

However, for the closed photobioreactor in the microalgal cultivation process, it is still common to supply CO_2 for microalgal growth during daylight [4,51,68]. Regardless of the systems for CO_2 distribution, most experiments do not consider the effect of gas losses to the atmosphere when a variety of CO_2 concentrations are used. Regarding the study by Rubio et al. [74], diffusion through tiny holes can offer better CO_2 mixing but it may not eliminate CO_2 losses. Thus, a higher cost is developed and increased levels of CO_2 released to the atmosphere will subsequently increase the air emission problem. Although a number of studies [71,80] have worked on controls to sufficiently distribute the CO_2 concentration (e.g. the supply of high CO_2 concentrations at midday), CO_2 losses cannot be abolished because of the CO_2 that is not consumed by the microalgae. Even though a hollow fiber membrane has been proposed in order to improve the mass transfer of CO_2, there is still a need for improvements to the CO_2 feedstock to avoid CO_2 generation into the atmosphere [41,78]. In view of this, the design of a system that captures CO_2 from the air as the CO_2 feedstock is addressed here. Carbon dioxide feedstock from the atmosphere can assure better microalgal growth while reducing CO_2 emissions to the atmosphere, which should help to halt the global warming issue, as mentioned previously.

4. Capturing carbon dioxide from the air

Capturing CO_2 from the air has been studied for decades in the context of producing CO_2-free air [32]. In addition, the purpose is to collect CO_2 as reasonably as possible and to store it for variety of purposes. The initiative of capturing CO_2 from the air becomes more complicated and requires more efficiently developed technology when the CO_2 concentration in the gas stream is very low. Indeed, the CO_2 content in air is approximately 400 ppm by

volume, as discussed earlier. Such a high degree of CO_2 dilution limits the practical capture options of sorption approaches [25]. However, many considerations need to be looked at first, such as the energy cost required for the absorption and desorption of CO_2 gas and the ability of the capturing system to accumulate the CO_2 to be used in future works. Furthermore, the material must reasonably easy to use and safe under the environmental conditions studied. In this section, we intend to distinguish the existing technologies of CO_2 capture from the air in terms of its availability and CO_2 accumulation possibilities and also its opportunity to provide CO_2 feedstock for microalgal cultivation.

4.1. Carbon dioxide enrichment technologies

The capture of CO_2 from the air is possible and necessary for achieving stabilization of the global CO_2 concentration in the atmosphere [81–83]. In addition, during photosynthesis, plants routinely use CO_2 from the air to provide energy, as stated previously. Furthermore, CO_2 in the air is not harmful and it is always available for microalgal cultivation. However, recovering CO_2 is not an easy task and it requires suitable technology for the separation of CO_2 to a recovery site. Two factors make the capture of CO_2 from the air require very adequate technology [27]: (1) a higher thermodynamic barrier due to the lower concentration of CO_2 in air; (2) the high energy and material costs of moving large quantities of air through the capturing process. Even the energy required to capture CO_2 from the air is huge (442–679 kJ/mol CO_2) and increases the separation costs; however, the capture of CO_2 from the air still remains as a priority for reducing emissions from sources of spread, such as factories and transportation [25,81,82,84]. Furthermore, many possible combinations of processes and separation methods can be conceived for CO_2 capture and recovery, as well.

Generally, the CO_2 capturing process can be undertaken by such technologies as shown in Table 2. As can be seen, capturing CO_2 by chemical absorption is based on the dissolution or solubility of a gas into the liquid phase. This process was discovered about half a century ago for the absorption of CO_2 from the air using an alkaline solution [98,99]. Recently, a number of researchers also dealt with this absorption process for capturing CO_2 from the air [20,84,100]. They normally used monoethanolamie (MEA), potassium hydroxide (KOH) or NaOH to capture CO_2 from the ambient atmosphere. These chemicals react with CO_2 molecules to form reacted CO_2, and the chemicals are then regenerated again using heat treatment. These processes are usually unprofitable. For instance, MEA desorption can typically constitute up to 70% of the total operating costs in a CO_2 capture plant [101]. Potassium hydroxide and NaOH may require temperatures of approximately 100 °C or above to regenerate the sorbents and the absorption processes are likely to be performed under pressurized conditions [84]. As higher temperature and pressurized condition are required, intensive energy inputs are desirable.

A second separation process is solid physical adsorption, which is known to be one of the most widespread commercial processes for gas purification and air separation on the small scale for atmospheric air. Adsorbents such as the X-type zeolite have been used for air purification by adsorbing CO_2 from ambient air, and they are then utilized for the separation of nitrogen and oxygen [89,102]. As well as showing a better performance in the adsorption of low concentrations of CO_2, this adsorbent also revealed an excellent function in absorbing higher CO_2 concentrations (up to 15%) to control CO_2 emissions [88,103,104]. In addition, the process of carbonation–calcination using calcium oxide (CaO) also revealed the ability to capture CO_2 from the air [26]. During this process, the reacted particles of CaO are transformed into calcium carbonate ($CaCO_3$) and CO_2-depleted air leaves the reaction site. Then, $CaCO_3$ is again transformed into CaO by the calcination reaction. However, according to Mérel et al. [91], the stronger the affinity (adsorbent), the more difficult it is to desorb the gas and, consequently, the heat energy required for recycling and reusing the adsorbent in the next cycle is increased. In the process of carbonation-calcination using CaO [81], although the carbonization step practically removes CO_2 from the air completely, the minimum temperature required for calcining the $CaCO_3$ is more than 800 °C.

It also has been shown that the capture of CO_2 from air is possible using a cryogenic plant and that it can be economical if a high CO_2 concentration of the feed (more than 20%) is applied [25,105]. This separation process is one of the most popular air separation processes, and it has been frequently used in medium to large-scale plants [93]. It is the most preferred technology for producing pure gaseous and liquid products. Furthermore, cryogenic separation is supposed to be the most cost effective technology for high quality gas and high production rate plants such as O_2 enrichment from air or capturing CO_2 from flue gas [106–108]. As a consequence, as high quality and high purity gases are produced (99.99% purity), more energy is consumed and may cost up to USD 37 million for complete process [95].

From these three separation technologies, it seems that chemical absorption and solid physical adsorption are reliable processes for capturing a low concentration of CO_2 from the air. However, the regeneration of chemicals and sorbent materials may reduce the benefits of both processes. Interestingly, researchers of gas separation technologies have quickly acquired or developed membrane-based processes to supplement older processing routes [109,110]. The multiple benefits of the CO_2 separation technology that were promised by early innovators have been proven in a variety of installations in many places around the world [111]. At the

Table 2
Description of CO_2 capture technologies.

Process	Descriptions	Operation	Capture	Disadvantages
Chemical absorption	Based on reaction or solubility of a gas and can be described by Henry's law [83]	Low temperature [10–50 °C] and will be regenerated at low pressure and temperatures ranging between 50 and 130 °C [85]	~50–95% [86]	Consumed higher energy for CO_2 recovery [87]
Solid physical adsorption	The CO_2 diffusion was controlled by micropore size and reactivity [88]	25 and 105 °C at pressure up to 15 bar [87]	~55–92% [89,90]	Increased the heat energy for recycling the adsorbent in the next cycle[92]
Cryogenic separation	Distillated component at a certain temperature and pressure [92]	Low as −100 °C, and at high pressure, almost 40 bars, to provide necessary removal of components [93,94]	More than 95% [93]	Required pilot plant scale which consumed more than USD 37 million [93]
Membrane separation	Separation depended on physical properties of gases [94]	Can be positioned either way with a multi-stage operation system without any separating agent[91]	~50–90% [95,96]	Low selectivity at high permeability [97]

moment, the most widely used membrane materials for gas separation are polymers [97]. Polymers are attractive materials for membranes because they are flexible enough to be processed into flat sheet membranes or hollow fiber membranes. The flat sheet membranes can be packaged as spiral-wound modules whereas the hollow fiber membranes can be arranged into a tube-and-shell configuration. Furthermore, polymers can also be easily used for various filtration process, such as microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO).

A number of membranes are commercially available for the separation of CO_2 and the subsequent treatment of global warming [97,112,113]. According to Brunetti et al. [111], although the membrane selectivity of CO_2 separation is almost 100, the permeability of CO_2 from flue gas is low. In general, the permeability of pure CO_2 (single gas) should be in the range of 1100–2200 Barrer (1 Barrer = 3.348×10^{-19} kmol m/(m^2 s Pa)) [97]. Thus, proper selection of the membrane material is extremely important as it can determine the ultimate performance of the gas separation module. Finally, the approach of membrane separation technologies for capturing CO_2 can offer several practical advantages, including high selectivity at low cost processes, and it has the potential to exert a positive influence on microalgal development.

4.2. Membrane separation for capturing carbon dioxide

Gas separation is usually achieved by physical or physicochemical phenomena. Over the past two decades, gas separation using polymeric membranes has drawn a great deal of interest from researchers due to its many advantages such as low energy costs and high selectivity. Furthermore, the polymer membrane seems to be selected more than other CO_2 separation processes since it is much safer and provides an easier separation process [114–117]. Up until recently, eight polymer materials have been commonly used for the CO_2 separation process [97]. Most separation processes are performed on homogenous dense membranes [14]. It has been reported that in order to capture CO_2, especially from the flue gas, a membrane should have the following properties, namely [97]:

(a) high permeability for pure CO_2 gas in the range of 1100–2200 Barrer;
(b) high CO_2/N_2 selectivity, for example the ideal selectivity of 1560 on the polyaniline membrane;
(c) thermal and chemical resistance to avoid membrane destruction at temperatures higher than 100 °C for flue gas treatment;
(d) plasticization resistance to avoid membrane swelling at pressures as high as 10 atm;
(e) aging resistance, which will maintain membrane separation performance each time;
(f) cost effective for developing a module or plant for CO_2 separation and treatment;
(g) the ability to be cheaply manufactured for different membrane modules and arrangements.

Generally, most polymeric membranes for CO_2/N_2 separations show CO_2/N_2 selectivity in the range of 5–50 [97]. Researchers have used liquid absorbents to improve membrane selectivity for CO_2 recovery. For example, Francisco and co-workers [118] used alkanolamine liquids to increase the CO_2/N_2 selectivity of a poly(vinyl alcohol) (PVA) membrane to more than 100. However, liquid absorbents always face difficulties such as liquid degradation, equipment corrosion and the release of volatile organic compounds [119]. It has been indicated that ionic liquids can offer a better solution for these difficulties and that they are more stable compared to conventional liquid absorbents [120]. According to Rahman et al. [121], ionic liquids also show good feasibility for the capture of CO_2 from air. Ionic liquids can be used to treat higher concentrations of CO_2, especially in flue gas. This is because CO_2 has high solubility in ionic liquids. For instance, CO_2 dissolved approximately a 0.2 molar fraction in 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], whereas other gases such as ethylene (C_2H_4), ethane (C_2H_6), methane (CH_4), argon (Ar) and oxygen (O_2) only dissolved less than a 0.1 molar fraction in the same ionic liquid [121]. Hence, it would be encouraging if these liquids could be solidified and grafted to a polymer membrane surface to enhance membrane selectivity and to avoid the leakage problems of liquid forms. In addition to great CO_2 absorption, solid absorbents allow only a slight loss compared to liquid forms when a certain temperature is applied [119]. Tang and co-workers [122] provided ionic liquids in a polymer form called poly(ionic liquid)s for CO_2 gas separation. These results showed that the adsorption ability of the poly(ionic liquid)s was up to 7 times greater than conventional ionic liquids. However, brittleness is the main problem with poly(ionic liquid) membranes. Despite showing a better performance at CO_2 absorption, poly(ionic liquid)s can be easily crushed at room temperature [119].

Recently, to the best of our knowledge, very limited work has been carried out on membrane separation for the capture of CO_2 from the ambient atmosphere, except for the separation of low concentrations of CO_2, especially in closed spaces [123–126]. Chen et al. [123] reported that the partial pressure of CO_2 in a closed space caused by breathing is around 0.005 atm or 0.5% of the CO_2 concentration. Conventionally, the separation process for this low concentration of CO_2 (0.5%) is performed by the adsorption/reaction using adsorbents/reagents which are discarded when saturated. As well as using adsorbents/reagents, Chen et al. [123] has used an immobilized liquid membrane, a glycerol-based liquid membrane, to improve membrane selectivity. As a result, the CO_2/N_2 separation factor at this low concentration (0.5% of CO_2) was observed to be over 5000 and it showed a stable performance even when the sweep gas was introduced. In our previous works [124–126], we attempted to use a hydrogel for membrane separation in order to increase membrane selectivity for separating low CO_2 concentrations. In these experiments, one of our group [125] has designed a system to remove CO_2 from the air using a polyvinylidene fluoride–polyvinyl acetate (PVDF–PVA) hydrogel membrane to replace conventional separation methods (i.e. absorption and adsorption). By using this PVDF–PVA hydrogel membrane, the CO_2 concentrations were reduced from 0.6–1.3% to 0.4–0.9% at the outlet stream. Other work in our group [124] used a hollow fiber-containing carbonic anhydrase (CA) hydrogel membrane contactor to recover the CO_2 concentration around to 0.52 vol%. As a result, the CO_2 concentration was reduced to less than 0.09% at the feed outlet [124]. Meanwhile, another effort [126] utilized a poly(acrylic acid-co-acrylamide)/hydrotalcite (PAA-AAm/HT) nanocomposite hydrogel which was filled between PVDF fibers to control the CO_2 concentrations in a closed life-support system. In this work, nearly 45% of the CO_2 was recovered from the inlet CO_2 concentrations in the range of 0.1–0.9%. Interestingly, the performance of a hydrogel as an active layer on the membrane's surface for the capture of CO_2 from ambient air can be induced. This is because these hydrogels (PVDF-PVA, CA, PAA-AAm/HT) have been shown to have the capability of absorbing low CO_2 concentrations (0.5–1%) [124–126]. Finally, this section shows that in order to integrate membrane separation into a photobioreactor, the membrane must be able to remove CO_2 from the air and capture low concentrations of CO_2 from the air. Then, the captured CO_2 will be accumulated for microalgal growth and consumption.

5. CO_2 capture and utilization by a selective integrated membrane photobioreactor

The term "integrated membrane system" is frequently used to describe a treatment system that incorporates membrane separation and available technologies in order to achieve a particular product or goal. In order to integrate membrane separation with an existing photobioreactor, the membrane separation process requires interdisciplinary research with contributions from biology, chemistry and physics. Integrated membrane systems have been applied for hydrogen production, CO_2 removal and for monitoring the optimal CO_2 concentration in bioreactors [127]. Our earlier works implemented the membrane separation process in a photobioreactor system to improve CO_2 distribution [33,41,78]. It is undoubtedly true that using membrane separation can increase CO_2 distribution in a microalgal medium. However, there is no improvement in atmospheric air since the source of CO_2 for microalgal cultivation has not been considered. In order to treat and improve atmospheric air with an existing system, capturing CO_2 via the membrane separation process is implemented by a photobioreactor system. It is believed that capturing CO_2 from the air via an integrated membrane separation photobioreactor will provide a continual CO_2 feedstock for the culture and will consume the CO_2 already added to the atmosphere without generating further CO_2 gas. Therefore, an appropriate and selective membrane for continuously capturing CO_2 needs to be developed where only low concentrations of CO_2 are available.

In order to continuously capture CO_2 using membrane separation, selective polymer membranes with a reversible CO_2 function are preferred. This is due to the low concentration of CO_2 in the atmosphere, which is not enough for microalgal cultivation. In principle, an amine with the $-NH_2$ functional group is always shows a reversible reaction for the absorption and desorption of CO_2 [86,87,118]. According to Xu et al. [128], an amine in the polymer form, polyethylenimine (PEI), also showed an excellent performance at capturing CO_2. Polyethylenimine, which has branches of $-NH_2$ functional groups, can react with CO_2 molecules to capture them. In comparison with a single functional group, branches of $-NH_2$ functional groups have the capability of spreading the CO_2 reaction in the polymer to capturing CO_2 from air. Thus, Xu et al. [128] recommended that in order to capture CO_2 continuously, PEI must be utilized in the membrane separation process. Other than this, ionic liquids, which can be switched to the polymer form, also have the functionality to absorb and to desorb CO_2 [121,122]. A previous experiment showed that when different pressures of feed and permeate sides are applied to a polyvinyl acetate (PVA) membrane comprising an alkanolamine liquid, CO_2 can be released from the carrier and a CO_2/N_2 selectivity of more than 100 can be achieved [118]. Thus, it can be accepted that the attachment of chemicals with a reversible CO_2 functionality on the surface of a membrane may show similar phenomena.

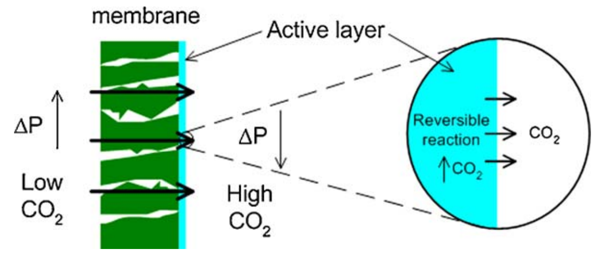


Fig. 3. Transport mechanism of CO_2 by selective membrane surface with reversible reaction.

Fig. 3 shows a concept of capturing CO_2 for enrichment by an active membrane surface. In this concept, the concentration of CO_2 from ambient air is fed through the membrane and the CO_2 penetrates through the active layer of the membrane. Interestingly, this concept uses pressure differences as the driving force allowing the permeation of CO_2 gas. In addition, the brittleness of the active support, such as poly(ionic liquid)s, can be avoided if supportive material is applied. For this reason, as can be seen, continuous CO_2 capture from the air is able to cooperate with microalgal cultivation for a continuous distribution of CO_2. The incorporation of the membrane separation process for capturing CO_2 while cultivating microalgae is a significant achievement. The process of selective membrane separation incorporating the photobioreactor process will be arranged as shown in Fig. 4. It is expected that with a selective membrane material and pressure differences as the driving force, the enriched CO_2 gas will permeate into the enriched CO_2 stream. Then, the enriched CO_2 gas will be distributed throughout the microalgal medium for the cultivation process. Afterwards, any unconsumed CO_2 will be recycled again to avoid CO_2 losses. In this schematic diagram, it is also recommended that the purity of the enriched CO_2 is controlled so that it stays at a certain concentration, for example, 1% CO_2, in order to cultivate microalgae such as *Chlorella vulgaris*. Finally, with these abilities, the system will be practical for capturing atmospheric CO_2 for microalgal cultivation systems in any land area.

The capture of CO_2 from the atmosphere for microalgal cultivation is still under development. However, this technology has extraordinary attention compare with technologies that already exist for cutting CO_2 emissions. Introducing CO_2 capture from the atmosphere for microalgal cultivation provides two important benefits. This capturing process not only reduces CO_2 levels in the air, but it is also a promising technology for providing suitable

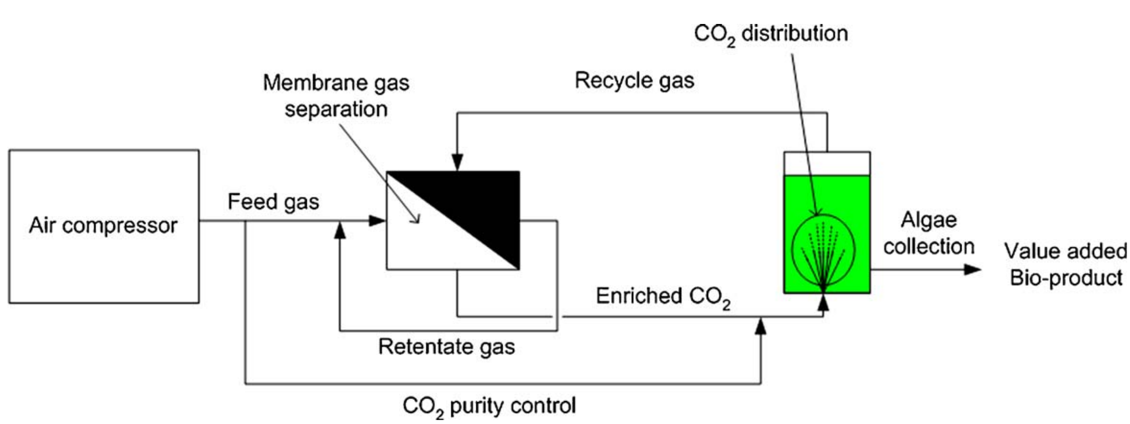


Fig. 4. Schematic of gas membrane separation incorporated photobioreactor on CO_2 enrichment process.

concentrations of CO_2 for microalgal development in order to gain the benefits from microalgal production.

6. Outlook

Capturing CO_2 from ambient air has been proven possible under atmospheric conditions. Although it has higher thermodynamic barrier and needs high energy and material costs, it provides a significant effort for managing carbon climate risks from spread sources. Regardless of using flue gases, it is beneficial if the CO_2 from ambient air can be used as a feedstock for microalgal cultivation processes. Despite the experience of CO_2 fixation in microalgal technology, many extraordinary challenges are involved in its operation. Low CO_2 concentration in the air (∼400 ppm), limits CO_2 utilization by microalgae. Moreover, unexpected CO_2 loses during microalgal cultivation must be fixed using enhanced CO_2 distribution systems. In addition, the inclusion of better CO_2 distribution systems have been introduced, an improvement allowing the microalgal cultivation process to be integrated with CO_2 capture from air. The membrane separation process is believed to be one of the most attractive technologies in terms of its advantages in dealing with the gas separation process. Because of the low concentration of CO_2 in the air, an active layer membrane with a continuously reversible CO_2 absorption and desorption function should be provided to increase the CO_2 capturing performance. Significantly, by introducing this membrane, the captured CO_2 can be utilized continuously in the microalgal cultivation process. Hence, microalgae in particular, could easily acquire the required CO_2 concentration even though only low CO_2 concentrations are available. The capture of CO_2 from air by an integrated membrane photobioreactor is still under development. There are some limitations which have to be considered, for example the accumulation potential for very diluted CO_2 concentrations (less than 400 ppm) and membrane fouling problems. Since microalgae use photosynthesis to consume CO_2 from the air, the process of capturing CO_2 from air could compensate for any emissions and, ideally, could be performed in any areas at any time.

Acknowledgements

This work is based upon research supported by the National Natural Science Foundation of China (No. 21076177), the Fundamental Research Funds for the Central Universities (2009QNA6007), the Zhejiang Provincial Natural Science Foundation of China (Y4100222) and Zhejiang Provincial Bureau of Education (Y201018490).

References

[1] Belay A, Ota Y, Miyakawa K, Shimamatsu H. Current knowledge on potential health benefits of spirulina. J Appl Phycol 1993;5:235–41.
[2] Ogbonda KH, Aminigo RE, Abu GO. Influence of temperature and pH on biomass production and protein biosynthesis in a putative Spirulina sp. Bioresour Technol 2007;98:2207–11.
[3] Yang C, Liu H, Ming L, Yu C, Yu G. Treating urine by Spirulina platensis. Acta Astronautica 2008;63:1049–54.
[4] Chisti Y. Biodiesel from microalgae beats bioethanol. Trends Biotechnol 2008;26:126–31.
[5] Chisti Y. Biodiesel from microalgae. Biotechnol Adv 2007;25:294–306.
[6] Dismukes CG, Carrieri D, Bennette N, Ananyey GM, Posewitz MC. Aquatic phototrophs, efficient alternatives to land-based crops for biofuels. Curr Opin Biotechnol 2008;19:235–40.
[7] Brennan L, Owende L. Biofuels from microalgae – a review of technologies for production processing and extractions of biofuels and co-products. Renew Sust Energ Rev 2010;14:557–77.
[8] Patil V, Tran KQ, Giselrød HR. Towards sustainable production of biofuels from microalgae. Int J Mol Sci 2008;9:1188–95.
[9] Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick Jr WJ, Hallett JP, Leak DJ, Liotta CL, Mielenz JR, Murphy R, Templer R, Tschaplinski T. The path forward for biofuels and biomaterials. Science 2006;311:484–9.
[10] Umdu ES, Tuncer M, Seker E. Transesterification of *Nannochloropsis oculata* microalga's lipid to biodiesel on Al_2O_3 supported CaO and MgO catalysts. Bioresour Technol 2009;100:2828–31.
[11] Chiu SY, Kao CY, Chen CH, Kuan TC, Ong SC, Lin CS. Reduction of CO_2 by a high-density culture of *Chlorella* sp. in a semicontinuous photobioreactor. Bioresour Technol 2008;99:3389–96.
[12] Keffer JE, Kleinheinz GT. Use of *Chlorella vulgaris* for CO_2 mitigation in a photobioreactor. J Ind Microbiol Biotechnol 2002;29:275–80.
[13] Xiong W, Gao C, Yan D, Wu C, Wu Q. Double CO_2 fixation in photosynthesis–fermentation model enhances algal lipid synthesis for biodiesel production. Bioresour Technol 2010;101:2287–93.
[14] Doucha J, Straka F, Livansky K. Utilization of flue gas for cultivation of microalgae *Chlorella* sp. in an outdoor open thin-layer photobioreactor. J Appl Phycol 2005;17:403–12.
[15] Doušková I, Kaštánek F, Maléterová Y, Kaštánek P, Doucha J, Zachleder V. Utilization of distillery stillage for energy generation and concurrent production of valuable microalgal biomass in the sequence Biogas-cogeneration-microalgae-products. Energ Convers Manage 2010;51:606–11.
[16] Nagase H, Yoshihara K, Eguchi K, Okamoto Y, Murasaki S, Yamashita R, Hirata K, Miyamoto K. Uptake pathway and continuous removal of nitric oxide from flue gas using microalgae. Biochem Eng J 2001;7:241–6.
[17] Yoo C, Jun SY, Lee JY, Ahn CH, Oh HM. Selection of microalgae for lipid production under high levels carbon dioxide. Bioresour Technol 2010;101:S71–4.
[18] Lee JS, Lee JP. Review of advanced biological of CO_2 in mitigation technology. Biotechnol Bioprocess Eng 2003;8:354–9.
[19] Sawayama S, Minowa T, Yokoyama SY. Possibility of renewable energy production and CO_2 mitigation by thermochemical liquefaction of microalgae. Biomass Bioenerg 1999;17:33–9.
[20] Baciocchi R, Storti G, Mazzotti M. Process design and energy requirements for the capture of carbon dioxide from air. Chem Eng Process 2006;45:1047–58.
[21] Yu KMK, Curcic I, Gabriel J, Tsang SCE. Recent advances in CO_2 capture and utilization. Chem Sus Chem 2008;1:893–9.
[22] Hansen J, Sato M, Ruedy R, Kharech P, Lacis A, Miller R, et al. Dangerous human-made interference with climate: a GISS modelE study. Atmos Chem Phys 2007;7:2287–312.
[23] World Population Prospects. The 2006 revision, highlights, working paper no. ESA/P/WP.202. United Nations, Department of economic and social affairs, Population division. New York; 2007.
[24] Florides GA, Christodoulides P. Global warming and carbon dioxide through sciences. Environ Int 2009;35:390–401.
[25] Mahmoudkhani M, Keith DW. Low-energy sodium hydroxide recovery for CO_2 capture from atmospheric air – thermodynamic analysis. Int J Greenhouse Gas Control 2009;3:376–84.
[26] Nikulshina V, Hirsch D, Mazzotti M, Steinfeld A. CO_2 capture from air and co-production of H_2 via the $CaOH_2$–$CaCO_3$ cycle using concentrated solar power-thermodynamic analysis. Energy 2006;31:1715–25.
[27] Keith D. Why capture CO_2 from the atmosphere. Science 2009;325:1654–5.
[28] Paris P, Rauer H, Grenfell JL, Patzer B, Hedelt P, Stracke B, et al. Warming the early earth-CO_2 reconsidered. Planet Space Sci 2008;56:1244–59.
[29] Barrie LA, Hoff RM. The oxidation rate and residence time of sulphur dioxide in the arctic atmosphere. Atmos Environ 1984;18:2711–22.
[30] Muzio LJ, Quartucy GC. Implementing NOx control: research to application. Prog Energ Combust Sci 1997;23:233–66.
[31] Beardall J, Raven JA. The potential effects of global climate change on microalgal photosynthesis growth and ecology. Phycologia 2004;43:26–41.
[32] Falkowski PG. The role of phytoplankton photosynthesis in global biogeochemical cycles. Photosynth Res 1994;39:235–58.
[33] Cheng LH, Zhang L, Chen HL, Gao CJ. Carbon dioxide removal from air by microalgae cultured in a membrane-photobioreactor. Sep Purif Technol 2006;50:324–9.
[34] Watanabe Y, Hall D. Photosynthetic CO_2 fixation technologies using a helical tubular bioreactor incorporating the filamentous cyanobacterium *Spirulina platensis*. J Ferment Bioeng 1996;81:470–2.
[35] Jeong ML, Gillis JM, Hwang JY. Carbon dioxide mitigation by microalgal photosynthesis. Bull Kor Chem Soc 2003;24:1763–6.
[36] Matsumoto H, Hamasaki A, Sioji N, Ikuta Y. Influence of CO_2, SO_2 and NO in flue gas on microalgae productivity. J Chem Eng Jpn 1997;30:620–4.
[37] Negoro M, Shioji N, Niyamoto K, Miura Y. Growth of microalgae in high CO_2 gas and effects of SOx, NOx. Appl Biochem Biotechnol 1991;28–29:877–86.
[38] Lee JN, Lee JS, Shin CS. Methods to enhance tolerances of Chlorella KR-1 to toxic compounds in flue gas. Appl Biochem Biotechnol 2000;84–86:329–42.
[39] Sung KD, Lee JS, Park SC, Choi MJ. CO_2 fixation by *Chlorella* sp. KR-1 and its cultural characteristics. Bioresour Technol 1999;68:269–73.
[40] Hirata S, Hayashitani M, Taya M, Setsuji T. Carbon dioxide fixation in batch culture of *Chlorella* sp. using a photobioreactor with a sunlight-collection device. J Ferment Bioeng 1996;81:470–2.
[41] Fan LH, Zhang YT, Zhang L, Chen HL. Evaluation of a membrane-sparged helical tubular photobioreactor for carbon dioxide biofixation by *Chlorella vulgaris*. J Membr Sci 2008;325:336–45.
[42] Hsueh HT, Li WJ, Chen HH, Chu H. Carbon bio-fixation by photosynthesis of *Thermosynechococcus* sp. CL-1 and *Nannochloropsis oculata*. J Photochem Photobiol B: Biol 2009;95:33–9.
[43] Jacob-Lopes E, Scoparo CHG, Lacerda LMCF, Franco TT. Effect of light cycles night/day on CO_2 fixation and biomass production by microalgae in photobioreactors. Chem Eng Process 2009;48:306–10.

[44] Meng X, Yang J, Xu X, Zhang L, Nie Q, Xian M. Biodiesel production from oleaginous microorganisms. Renew Energ 2009;34:1–5.
[45] Arief W, Chien CC, Ju YH. Study of increasing lipid production from fresh water microalgae *Chlorella vulgaris*. J Taiwan Inst Chem Eng 2009;40:3–20.
[46] Rao AR, Sarada R, Ravishankar GA. Influence of CO_2 on growth and hydrocarbon production in *Botryococcus braunii*. J Microbiol Biotechnol 2007;17:414–9.
[47] Singh Y, Kumar HD. Lipid and hydrocarbon production by *Botryococcus* spp. under nitrogen limitation and anaerobiosis. World J Microbiol Biotechnol 1992;8:121–4.
[48] Zepka LQ, Jacob-Lopes E, Goldbeck R, Queiroz MI. Production and biochemical profile of the microalgae *Aphanothece microscopica Nägeli* submitted to different drying conditions. Chem Eng Process 2008;47:1305–10.
[49] An JY, Lee JS, Kim BW. Hydrocarbon production from secondarily treated piggery wastewater by the green alga *Botryococcus braunii*. J Appl Phycol 2003;15:185–91.
[50] de Morais MG, Costa JAV. Carbon dioxide fixation by *Chlorella kessleri, C.vulgaris Scenedesmus obliquus* and *Spirulina* sp. cultivatedin flasks and vertical tubular photobioreactors. Biotechnol Lett 2007;29:1349–52.
[51] de Morais MG, Costa JAV. Isolation and selection of microalgae from coal fired thermoelectric power plant for biofixation of carbon dioxide. Energ Convers Manage 2007;48:2169–73.
[52] Miao XL, Wu QY. High yield bio-oil production from fast pyrolysis by metabolic controlling of *Chlorella protothecoides*. J Biotechnol 2004;110:85–93.
[53] Chiu SY, Kao CY, Tsai MT, Ong SC, Chen CH, Lin CS. Lipid accumulation and CO_2 utilization of *Nannochloropsis oculata* in response to CO_2 aeration. Bioresour Technol 2009;100:833–8.
[54] Guo Z, Chen Z, Zhang W, Yu X, Jin M. Improved hydrogen photoproduction regulated by carbonylcyanide m-chlorophenylhrazone from marine green alga *Platymonas subcordiformis* grown in CO_2-supplemented air bubble column bioreactor. Biotechnol Lett 2008;30:877–83.
[55] Xie J, Zhang Y, Li YG, Wang YG. Mixotrophic cultivation of *Platymonas subcordiformis*. J Appl Phycol 2001;13:343–7.
[56] Gouveia L, Oliveira AC. Microalgae as a raw material for biofuels production. J Ind Microbiol Biotechnol 2009;36:269–74.
[57] Baker EW. Microalgae biotechnology and microbiology. In: Baddiley J, Carey NH, Higgins IJ, Potter WG, editors. Cambridge Studies in Biotechnology, vol. 10. Cambridge NY: Cambridge Univ. Press; 1994. p. 43–178.
[58] Pulz O, Gross W. Valuable products from biotechnology of microalgae. Appl Microbiol Biotechnol 2004;65:635–48.
[59] Tamiya H, Hase E, Shibata K, Mituya A, Iwamura T, Nihei T, Sasa T. Kinetics of growth of Chlorella with special reference to its dependence on quantity of available light and on temperature. In: Burlew JS, editor. Algal Culture from Laboratory to Pilot Plant. Washington, DC: Carnegie Inst Washington; 1953. p. 204–32.
[60] Ugwu CU, Ogbonna JC, Tanaka H. Light/dark cyclic movement of algal culture *Synechocystis aquatilis*. In outdoor inclined tubular photobioreactor equipped with static mixers for efficient production of biomass. Biotechnol Lett 2005;27:75–8.
[61] Jorquera O, Kiperstok A, Sales EA, Embiruçu M, Ghirardi ML. Comparative energy life-cycle analyses of microalgal biomass production in open ponds and photobioreactors. Bioresour Technol 2010;101:1406–13.
[62] Laws EA, Taguchi S, Hirata J, Pang L. Optimization of microalgal production in a shallow outdoor flume. Biotechnol Bioeng 1988;32:140–7.
[63] Richmond A, Boussiba S, Vonshak A, Kopel R. A new tubular reactor for mass production of microalgal outdoors. J Appl Phycol 1993;5:327–32.
[64] Lehr F, Posten C. Closed photo-bioreactors as tools for biofuel production. Curr Opin Biotechnol 2009;20:280–5.
[65] Suh IS, Lee CG. Photobioreactor engineering design and performance. Biotechnol Bioprocess Eng 2003;8:313–21.
[66] Sánchez GJL, Berenguel M, Rodríguez F, Sevilla FJM, Alias BC, Fernández AFG. Minimization of carbon losses in pilot-scale outdoor photobioreactors by model-based predictive control. Biotechnol Bioeng 2003;84:532–43.
[67] Raven JA. Inorganic carbon concentrating mechanisms in relation to the biology of algae. Photosynth Res 2003;77:155–71.
[68] Tsoglin LN, Gabel BV, Fal'kovich TN, Semenenko VE. Closed photobioreactors for microalgal cultivation. Russ J Plant Physiol 1996;43:131–6.
[69] Dutil F. Photobioreactor. US Patent 2003073231A1; 2003.
[70] Craigie JS, Amstrong SM, Staples LS, Bauder AG. Photobioreactor. US Patent 2003059932A1; 2003.
[71] Contreras A, García F, Molina E, Merchuk JC. Interaction between CO_2-mass transfer light availability and hydrodynamic stress in the growth of *Phaeodactylum tricornutum* in a concentric tube airlift photobioreactor. Biotechnol Bioeng 1998;60:317–25.
[72] Levin A. Photobioreactor. US Patent 2007155006A1; 2007.
[73] Zijffers JWF, Janssen M, Tramper J, Wijffels RH. Design process of an area-efficient photobioreactor. Mar Biotechnol 2008;10:404–15.
[74] Rubio FC, Fernández AFG, Pérez SJA, Camacho G, Grima M. Prediction of dissolved oxygen and carbon dioxide concentration profiles in tubular photobioreactors for microalgal culture. Biotechnol Bioeng 1999;62:72–86.
[75] Chisti Y. Airlift bioreactor. London: Elsevier; 1989.
[76] Lee YK, Hing HK. Supplying CO_2 to photosynthetic algal cultures by diffusion through gas-permeable membranes. Appl Microbiol Biotechnol 1989;31:298–301.
[77] Carvalho PA, Malcata X. Transfer of carbon dioxide within cultures of microalgae plain bubbling versus hollow-fiber modules. Biotechnol Prog 2001;7:265–72.
[78] Fan LH, Zhang YT, Cheng LH, Zhang L, Tang DS, Chen HL. Optimization of carbon dioxide fixation by *Chlorella vulgaris* cultivated in a photobioreactor. Chem Eng Technol 2007;30:1094–9.
[79] Greenwell HC, Laurens LML, Shields RJ, Lovitt RW, Flynn KJ. Placing microalgae on the biofuels priority list: a review of the technological challenges. J R Soc Interface 2010;7:703–26.
[80] Sobczuk MT, Camacho GF, Rubio CF, Fernández AFG, Grima ME. Carbon dioxide uptake efficiency by outdoor microalgal cultures in tubular airlift photobioreactors. Biotechnol Bioeng 2000;62:465–75.
[81] Nikulshina V, Gebald C, Steinfeld A. CO_2 capture from atmospheric air via consecutive CaO-carbonation and $CaCO_3$-calcination cycles in a fluidized-bed solar reactor. Chem Eng J 2009;146:244–8.
[82] Zeman F. Energy and material balance of CO_2 capture from ambient air. Environ Sci Technol 2007;41:7558–63.
[83] Zhang L, Siepmann JI. Direct calculation of Henry's law constants from Gibbs ensemble monte carlo simulations nitrogen, oxygen, carbon dioxide and methane in ethanol. Theor Chem Acc 2006;115:391–7.
[84] Mahmoudkhani M, Heidel KR, Ferreira JC, Keith DW, Cherry RS. Low energy packed tower and caustic recovery for direct capture of CO_2 from air. Energy Procedia 2009;1:1535–42.
[85] Palmeri N, Cavallaro S, Bart JCJ. Carbon dioxide absorption by MEA – a preliminary evaluation of a bubbling column reactor. J Therm Anal Calorim 2008;91:87–91.
[86] Wang B, Jin H, Zheng D. Recovery of CO_2 with MEA and K_2CO_3 absorption in the IGCC system. Int J Energy Res 2004;28:521–35.
[87] Yang H, Xu Z, Fan M, Gupta R, Slimane RB, Bland AE, Wright I. Progress in carbon dioxide separation and capture – a review. J Environ Sci 2008;20:14–27.
[88] Liang Z, Marshall M, Chaffee AL. Comparison of Cu-BTC and zeolite 13X for adsorbent based CO_2 separation. Energy Procedia 2009;1:1265–71.
[89] Rege SU, Yang RT, Buzanowski MA. Sorbents for air prepurification in air separation. Chem Eng Sci 2000;55:4827–38.
[90] Wang M, Lee CG. Absorption of CO_2 on $CaSiO_3$ at high temperatures. Energ Convers Manage 2009;50:636–8.
[91] Mérel J, Clausse M, Meunier F. Carbon dioxide capture by indirect thermal swing adsorption using 13X zeolite. Environ Prog 2006;25:327–33.
[92] Olajire AA. CO_2 capture and separation technologies for end-of-pipe applications – a review. Energy 2010;35:2610–28.
[93] Hart A, Gnanendran N. Cryogenic CO_2 capture in natural gas. Energy Procedia 2009;1:697–706.
[94] White V, Torrente-Murciano L, Sturgeon D, Chadwick D. Purification of oxyfuel-derived CO_2. Energy Procedia 2009;1:399–406.
[95] Paranjape M, Clarke PF, Pruden BB. Separation of bulk carbon dioxide-hydrogen mixtures by selective surface flow membrane. Adsorption 1998;4:355–60.
[96] Stewart C, Hessami MA. A study of methods of carbon dioxide capture and sequestration-the sustainability of a photosynthetic bioreactor approach. Energ Convers Manage 2005;46:403–20.
[97] Powell CE, Qiao GG. Polymeric CO_2/N_2 gas separation membranes for the capture of carbon dioxide from power plant flue gases. J Membr Sci 2006;279:1–49.
[98] Spector NA, Dodge BF. Removal of carbon dioxide from atmospheric air. Trans Am Inst Chem Eng 1946;42:827–48.
[99] Tape JB, Dodge BF. Absorption of carbon dioxide by sodium hydroxide solutions in a packed column. Trans Am Inst Chem Eng 1943;39:255–76.
[100] Belmabkhout Y, Serna-Guerrero R, Sayari AH. Amine-bearing mesoporous silica for CO_2 removal from dry and humid air. Chem Eng Sci 2010;65:3695–8.
[101] Idem R, Wilson M, Tontiwachwuthikul P, Chakma A, Veawab A, Aroonwilas A, et al. Pilot plant studies of the CO_2 capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO_2 capture technology development plant and the boundary dam CO_2 capture demonstration plant. Ind Eng Chem Res 2006;45:2414–20.
[102] Rege SU, Yang RT, Qian K, Buzanowski MA. Air-prepurification by pressure swing adsorption using single/layered beds. Chem Eng Sci 2001;56:2745–59.
[103] Chatti R, Bansiwal AK, Thote JA, Kumar V, Jadhav P, Lokhande SK, et al. Amine loaded zeolites for carbon dioxide capture amine loading and adsorption studies. Micropor Mesopor Mater 2009;121:84–9.
[104] Jadhav PD, Chatti RV, Biniwale RB, Labhsetwar NK, Devotta S, Rayalu SS. Monoethanol amine modified zeolite 13X for CO_2 adsorption at different temperatures. Energy Fuels 2007;21:3555–9.
[105] Steeneveldt R, Berger B, Torp TA. CO_2 capture and storage closing the knowing-doing gap. Chem Eng Res Des 2006;84:739–63.
[106] Burdyny T, Struchtrup H. Hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process. Energy 2010;35:1884–97.
[107] Tuinier MJ, van Sint Annaland M, Kramer GJ, Kuipers JAM. Cryogenic CO_2 capture using dynamically operated packed beds. Chem Eng Sci 2010;65:114–9.
[108] Zanganeh KE, Shafeen A, Salvador C. CO_2 capture and development of an advanced pilot-scale cryogenic separation and compression unit. Energy Procedia 2009;1:247–52.
[109] Rao MB, Sircar S. Nanoporous carbon membranes for separation of gas mixtures by selective surface flow. J Membr Sci 1993;85:253–64.
[110] Rao MB, Sircar S. Performance and pore characterization of nanoporous carbon membranes for gas separation. J Membr Sci 1996;110:109–18.

[111] Brunetti A, Scura F, Barbieri G, Drioli E. Membrane technologies for CO_2 separation. J Membr Sci 2009;1–2:115–25.
[112] Baker RW. Future directions of membrane gas separation technology. Ind Eng Chem Res 2002;41:1393–411.
[113] Yazawa T, Kishimoto M, Inoue T, Mineshige A, Kobune M, Kuraoka K. Preparation of CO_2-selective separation membranes with highly chemical and thermal stability prepared from inorganic–organic nanohybrids containing branched polyethers. J Mater Sci 2007;42:723–7.
[114] Baker RW, Lokhandwala K. Natural gas processing with membranes. An overview. Ind Eng Chem Res 2008;47:2109–21.
[115] Durgar'yan SG, Yampol'skii YP, Plate NA. Selectively permeable polymers and gas-separation membranes structure and transport properties. Russ Chem Rev 1988;57:974–89.
[116] Liu L, Chakma A, Feng X. CO_2/N_2 separation by polyether block amide thin film hollow fiber composite membranes. Ind Eng Chem Res 2005;44:6874–82.
[117] Maier G. Gas separation with polymer membranes. Angew Chem Int Ed 1998;37:2674–960.
[118] Francisco GJ, Chakma A, Feng X. Membranes comprising of alkanolamines incorporated into polyvinyl alcohol matrix for CO_2/N_2 separation. J Membr Sci 2007;303:54–63.
[119] Tang J, Sun W, Tang H, Radosz M, Shen Y. Enhanced CO_2 absorption of poly(ionic liquid)s. Macromolecules 2005;8:2037–9.
[120] Kim YS, Yang SM. Absorption of carbon dioxide through hollow fiber membranes using various aqueous absorbents. Sep Purif Technol 2000;21:101–9.
[121] Rahman HM, Siaj M, Larachi F. Ionic liquids for CO_2 capture – development and progress. Chem Eng Process 2010;49:313–22.
[122] Tang J, Tang H, Sun W, Plancher H, Radosz M, Shen Y. Poly(ionic liquid)s a new material with enhanced and fast CO_2 absorption. Chem Commun 2005;332:5–3327. DOI: 10.1039/b501940k.
[123] Chen H, Obuskovic G, Majumdar S, Sirkar KK. Immobilized glycerol-based liquid membranes in hollow fibers for selective CO_2 separation from CO_2–N_2 mixtures. J Membr Sci 2001;183:75–88.
[124] Cheng LH, Zhang L, Chen HL, Gao CJ. Hollow fiber contained hydrogel-CA membrane contactor for carbon dioxide removal from the enclosed spaces. J Membr Sci 2008;324:33–43.
[125] Xu L, Zhang L, Chen HL. Study on CO_2 removal in air by hydrogel membranes. Desalination 2002;148:309–13.
[126] Zhang YT, Zhang L, Chen HL, Zhang HM. Selective separation of low concentration CO_2 using hydrogel immobilized CA enzyme based hollow fiber membrane reactors. Chem Eng Sci 2010;65:3199–207.
[127] Gassanova LG, Netrusov AI, Teplyakov VV, Modigell M. Fuel gases from organic wastes using membrane bioreactors. Desalination 2006;198:56–66.
[128] Xu X, Song C, Andresen MJ, Miller GB, Scaroni WA. Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO_2 capture. Energy Fuels 2002;16:1463–9.